INFERENCES ON THE STRUCTURE OF COAL: ^{13}C NMR AND IR SPECTROSCOPY

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INTRODUCTION

The low solubility of coal in suitable nmr solvents (1) has limited high resolution nmr studies of coal to solvent extracts not necessarily representative of coal structure, or to extreme techniques (pyrolytic hydrogenation, high temperature distillation) which cast doubt on the structural memory of the resulting solutions. Nondestructive wideline nmr (2,3) produces little or no useful spectral information due to severe loss of resolution and fine structure. The same objections hold for infrared studies;thenondescript complexity of ir spectra of coal has made them useful in only the most qualitative sense. A mild technique for the dissolution of coal with minimal loss of structural memory is thus vital for the successful application of nmr and ir to coal-structure elucidation. The acid-catalyzed depolymerization of coal by phenol, used by Ouchi and Brooks (4) to dissolve 87% of a depolymerized Yallourn brown coal sample in methanol,appeared highly attractive for this purpose. We present the first account, to our knowledge, of the application of ^{13}C nmr and ir spectroscopy for monitoring the successive dissolution of coal under mild conditions. Spectroscopic results, analytical and radiochemical data are presented which depict the structural changes occurring during depolymerization and permit tentative identification of structural types.

EXPERIMENTAL

SUCCESSIVE DEPOLYMERIZATION OF KNIFE RIVER COAL. A procedure similar to that of Ouchi (4, 5) was used for the depolymerization of Knife River coal whose elemental analysis can be found in Table II. Knife River coal (Beulah, Mercer Co., North Dakota) is classified as a lignite. After drying, elemental analysis and calorimetry permit assignment to the A.S.T.M. rank of high-volatile bituminous C. In a typical experiment, coal (10.7 g, dry basis), phenol (55.6 g), and p-toluenesulfonic acid (PTSA) were combined in a 3-neck, round-bottom flask equipped with mechanical stirrer, heating mantle, thermometer, and reflux condenser. Heating and stirring was begun without the reflux condenser until water contained in the coal and PTSA was driven off. The reflux condenser was attached, and the reaction proceeded at 185° for 6 hr. Phenol was removed by steam distillation. The resulting powder was filtered and washed thoroughly with water to remove PTSA and dried at 10^{-1} Torr and 125° for 10 hr. Soxhlet extraction of the depolymerized coal with methanol yielded a methanol soluble material (MeOH extract #1, nmr-1, ir-1a) and an insoluble material (residue #1, ir-1b). The procedure was repeated twice, substituting the insoluble residue after methanol extraction each time for coal. Results are summarized in Table 1.

Table 1 - Summary of Successive Depolymerization Steps

Step No.	Wt Initial Mat'l	Wt Depolymerisate	Wt Extract	Wt Residue	Corrected Wt Extract‡	Accumulated % Coal Extracted‡
1	10.70	13.26	4.97[a]	8.29[b]	2.30	21.5
2	8.29	10.93	4.37[c]	6.62[d]	2.72	46.9
3	6.62	8.85	3.01[e]	5.87[f]	1.66	62.4
1A	4.1056	5.9913	2.24	3.76	1.12	27.3

‡Correction based on assumption that 59.3% of the phenol taken up during depolymerization is MeOH soluble. This percentage derives from the ^{14}C experiment described below. a-nmr-1, ir-1a; b-ir-1b; c-nmr-2, ir-2a; d-ir-2b; e-nmr-3, ir-3a; f-ir-3b.

DEPOLYMERIZATION OF KNIFE RIVER COAL USING 1-^{14}C PHENOL. In experiment 1A of Table 1, a sample of Knife River coal, 4.1056 g (dry basis) was stirred with a mixture of p-toluenesulfonic acid (PTSA) (5.79 g) and 50.7 g of phenol exhibiting 3.9 $\pm$ 0.1 x 10^6 disintegrations min^{-1} g^{-1} (determined by scintillation counting) for 6 hr at 185° (reflux temperature of phenol). Unreacted phenol was removed by steam distillation, the resulting powder was filtered and washed thoroughly with water to remove PTSA. The depolymerized coal exhibited 12.3 $\pm$ 0.2 x 10^5 d min^{-1} g^{-1} of activity. Extraction with methanol left an insoluble residue exhibiting 7.4 $\pm$ 0.1 x 10^5 d min^{-1} g^{-1} activity and a methanol soluble fraction exhibiting 18.1 $\pm$ 0.3 x 10^5 d min^{-1} g^{-1} activity. ^{14}C combustion analysis established 0.71 g phenol contained in the residue, and 1.04 g of phenol contained in the extract. Elemental analyses were performed by the Schwarzkopf Analytical Laboratories.

Table 2 - Elemental Analyses

Sample	C	H	N	S	O	Atomic H/C	Corrected H/C†
Knife River coal	61.84	4.12	0.49	0.70	29.31	0.785	
Successive Depolymerization							
MeOH Extract #1	75.54	4.82	0.35	1.84	16.52	.758	0.474
MeOH Extract #2	73.40	4.70	0.35	3.53	15.65	.761	0.604
MeOH Extract #3	75.06	5.92	0.09	2.75	16.45	.939	0.880
Residue #1	73.28	4.16	0.58	2.37	16.36	.675	0.579
Residue #2	71.85	3.84	0.35	1.35	14.86	.634	0.740
Residue #3	71.88	4.03	0.40	1.50	14.23	.668	0.600

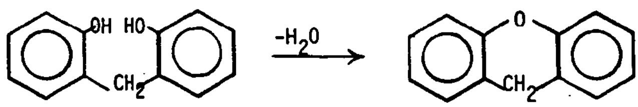
†The corrected H/C ratio was calculated using the distributive results of the ^{14}C experiment to correct for phenol uptake by both residue and extract. It was assumed that 40.7% of the phenol remained in the residue and the remainder went with the extract in each successive depolymerization. Of course, this assumption must be accepted only with reservation.

^{13}C NMR SPECTRA AND IR SPECTRA. Proton-decoupled ^{13}C nmr spectra were determined at the University of Utah with a Varian Associates XL-100 FTNMR Spectrometer operating at 25.16 MHz. Dioxane was used as an internal lock signal. Methanol solutions of Extracts 1, 2, and 3 contained no nonbonded phenol (gc analysis) and no PTSA (by addition of authentic sample to nmr tube). Infrared spectra were determined by a computer-coupled Perkin-Elmer model 521 Spectrometer. KBr pellets containing 0.5% sample concentration by weight were used. See Figure 1 for ^{13}C nmr spectra and Figures 2 and 3 for ir spectra.

DISCUSSION

The ^{13}C nmr spectra of Extracts 1, 2, and 3 are shown in Figure 1. Since the depolymerization procedure incorporated bonded phenol into the coal structure, there is some uncertainty as to the percent of coal actually dissolved. However, at least 45% of the original coal was depolymerized and extracted assuming the worst case that all of the phenol ended up in the extracts. The actual quantity is greater since the weight gain on depolymerization occurs by incorporation of phenol in both residue and extract. To estimate the partitioning of phenol between residue and extract, ^{14}C-labeled phenol was used in a depolymerization. If the distribution of phenol determined in the labeling experiment can be extrapolated to later stages of a successive depolymerization, then up to 62% of coal structure is contained in the methanol extracts. Reliable data for such an extrapolation must await further labeling studies. Nevertheless, a significant portion of the coal structure has been successfully dissolved.

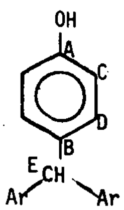
The general features of the ^{13}C nmr and ir spectra of Knife River coal residues and extracts indicate an aromatic system with high phenolic/hydroxylic OH content, modest aliphatic structure, and very little carbonyl content. The overall features of the ir spectrum of the original coal (ir-4) are retained on depolymerization, in accordance with the observations of Ouchi (5) using brown coal. Elemental analysis reveals a substantial drop in oxygen content, in the first depolymerization step, attributed (4) to dehydration reactions of the type

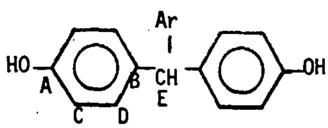


A four to five-fold increase in aliphatic CH content occurs in the methanol extracts from the first to third depolymerization. This is indicated by the increase in CH aliphatic stretching bands from 2800 to 3000 cm^{-1} in ir spectra ir-1a through ir-3a. At the same time, the aromatic C=C stretching bond at $\sim$1600 cm^{-1} decreases from extract 1 to 3. The increase in aliphatic CH is accompanied by a significant increase in the H/C ratio (from elemental analysis) in the extracts of successive depolymerizations. The apparent change in aliphatic content in residues 1-3 appears to be small, and carbonyl content ($\sim$1750 cm^{-1}) is concentrated in the residues. All of these observations parallel those of Ouchi (5) who found that aliphatic structure increases in the extracts, and that the residues show an increasingly dense network of aromatic structure.

The ^{13}C nmr spectra (Figure 1) of Extracts 1-3 show a similar pattern. Nmr-1 of Extract #1 shows a complex aromatic structure (4200-2800 Hz, 167-111 ppm) with a much smaller complement of aliphatic structure, most apparent in the region 900-300 Hz (36-12 ppm). Aliphatic resonances at ca. 830 Hz (33 ppm) in nmr 1-3 can be tentatively assigned to aliphatic methine and/or methylene bridge carbons (Ar_2CH_2 or Ar_3CH). The resonances at ca.600 Hz (23.9 ppm) can be assigned to methyl groups attached to aromatic nuclei (6,7). No long-chain aliphatic, olefinic or carbonyl resonances are detectable.

The nmr spectra of successive extracts show a decrease in aromatic/aliphatic content, in agreement with infrared and analytical data. The aromatic regions become progressively simpler with successive extracts. At the third stage, the aromatic region of the spectrum suggests a highly specific reaction and extraction sequence, yielding a mixture of highly similar structures. Nmr-2 is consistent with the general structures 1 or 2: The quaternary carbons A (3945 Hz, 156.8 ppm) and

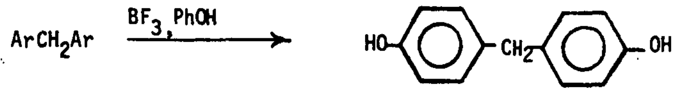




B (3630 Hz, 144.3 ppm) are unaffected in an off-resonance experiment, while aromatic methines C (3255 Hz, 129.4 ppm), and D (2925 Hz, 116.2 ppm) and aliphatic methine E (820 Hz, 32.6 ppm) become doublets. Complex structure surrounding the doublet in the off-resonance experiment provides evidence for aromatic methylene groups as well as methine E at 33 ppm.

In addition, a quaternary aliphatic carbon appears at 1095 Hz (43.5 ppm) in nmr-3. Precise structural assignment has not been made at the time of writing. Detectable aromatic structure probably associated with this resonance has not been identified.

The genesis of structures 1 and/or 2 (Ar = coal-derived structure) may be consistent with an increasingly endothermic depolymerization reaction reflected in a much greater specificity in point of attack on the coal structure. Structure 2 may result from displacement of two aromatic moieties from a ArCH group. A closely related reaction has been used to extract methylene groups from model compounds (Ar, CH_2Ar_2) and from coal:[8]



SUMMARY

A modified method of Ouchi and Herédy for depolymerizing coal shows great promise for obtaining substantial fractions in true solutions. These solutions can be used in high resolution ^{13}C nmr studies and in infrared studies to elucidate the basic structures of coals.

The technique has been demonstrated for a high-volatile bituminous C coal. We are currently pursuing this research in an attempt to obtain structural information, particularly with emphasis on the functional groups in coal and their effect on its reactivity.

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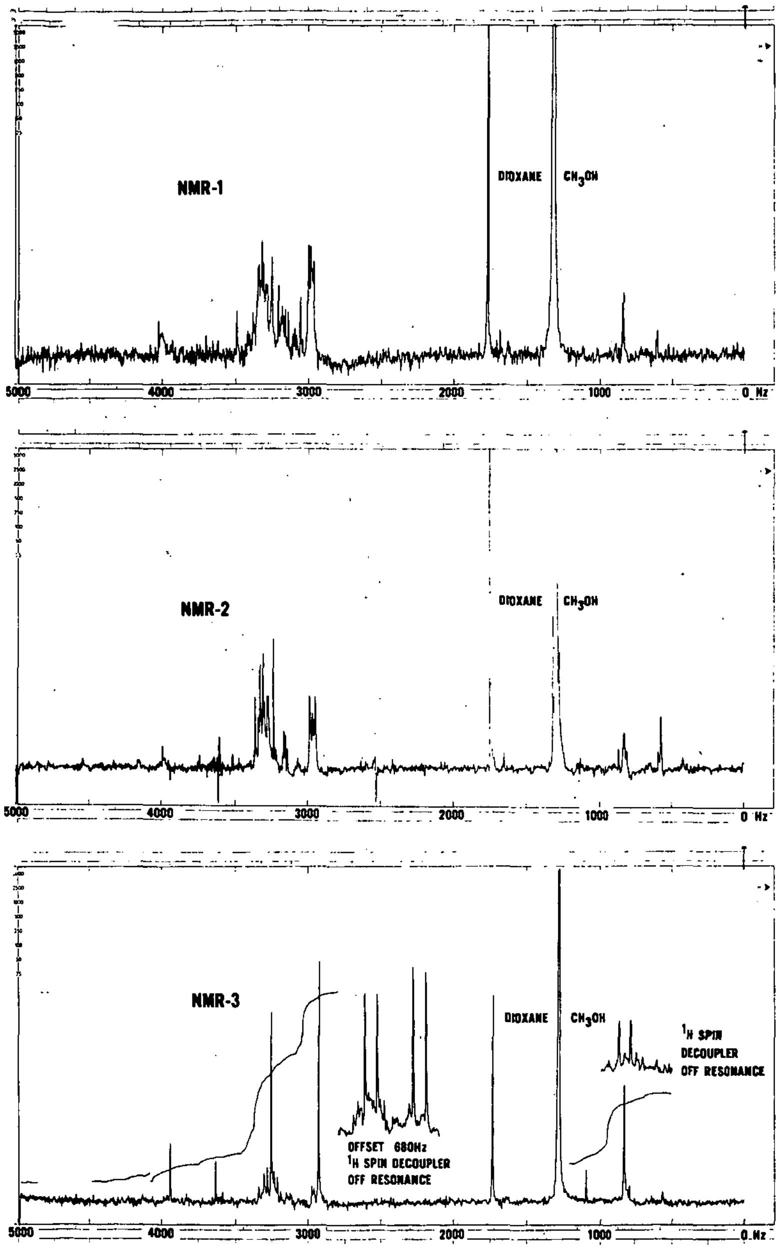

Figure 1. ^{13}C NMR Spectra of CH_3OH-soluble Fractions from the Successive Depolymerization of Knife River Coal.

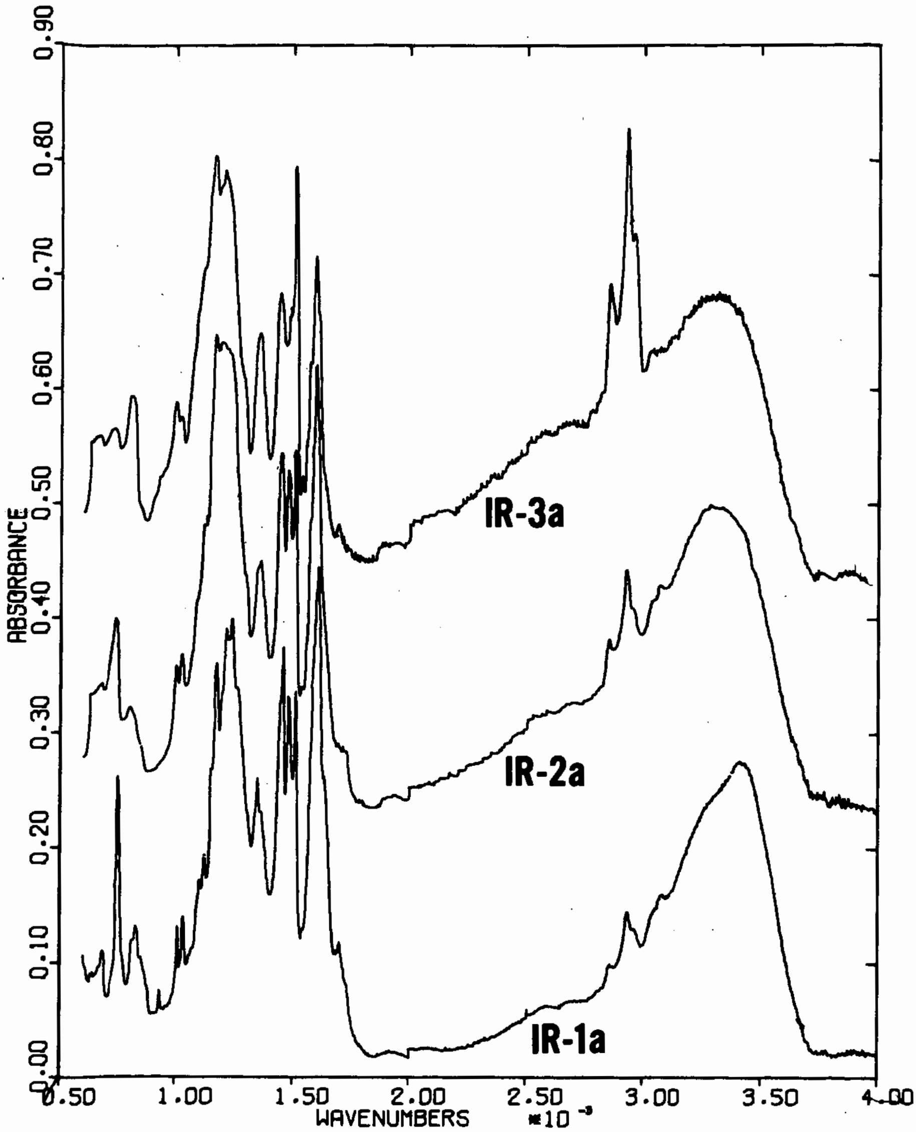

Figure 2. Infrared Spectra of CH_3OH Fractions from the Successive Depolymerization of Knife River Coal.

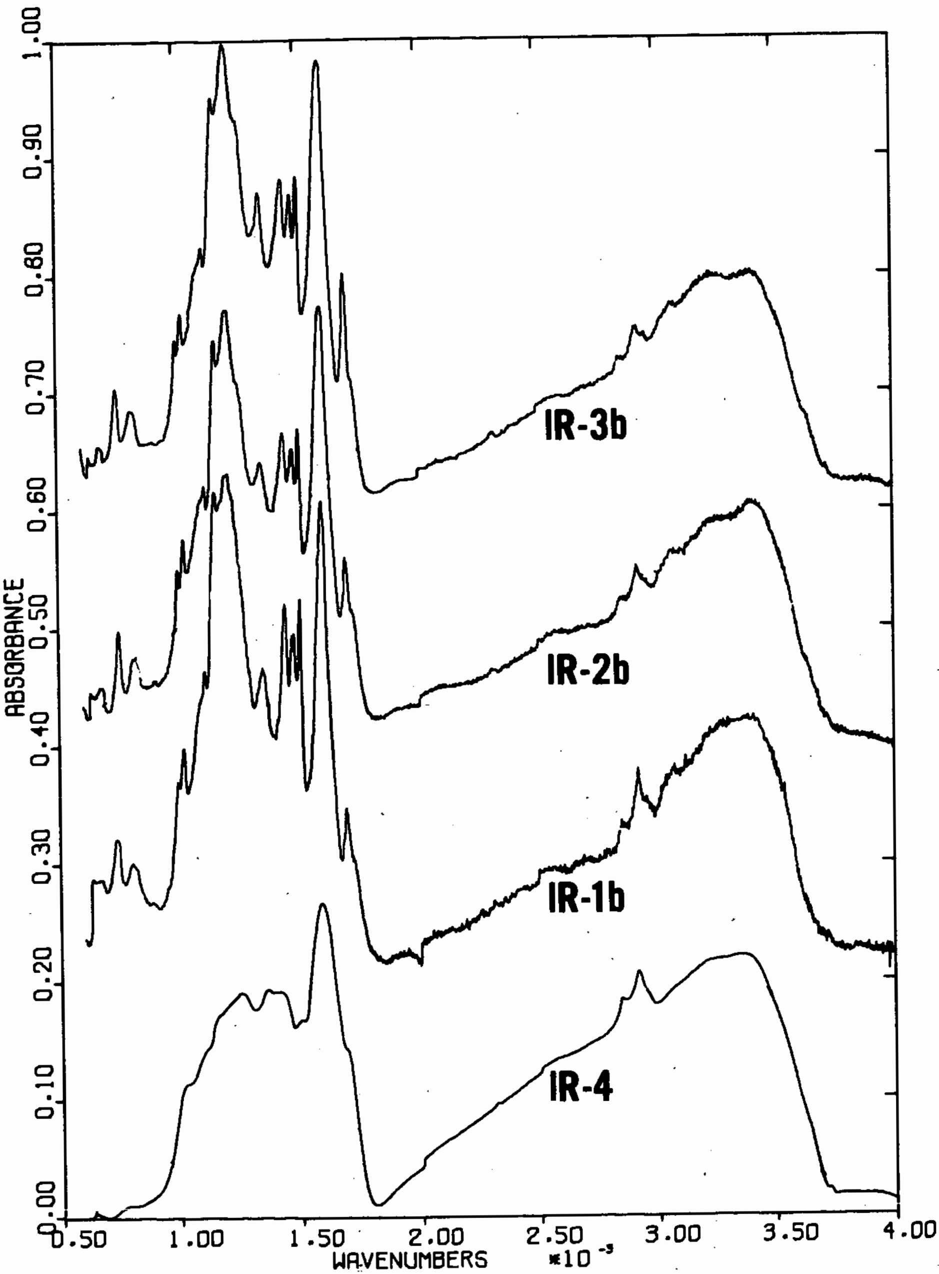

Figure 3. Infrared Spectra of Residues from the Successive Depolymerization of Knife River Coal (ir-1b, 2b, 3b) and of Knife River Coal (ir-4).